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Short Communication

Simple, Selective and Non-Extractive Spectrophotometric Determination of Co (II) Using 2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone

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ABSTRACT

2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone (AHNH) is a new chromogenic reagent used for the determination of cobalt (II) by simple, rapid, sensitive, selective, direct and derivative spectrophotometricmethod. 2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone forms a light pink coloured Co (II) - 2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone complex shows maximum absorbance at 450 nm at pH 2.0. The reagent blank shows negligible absorbance. Hence, the analytical studies were carried out at 450nm. The method obeyed Beer's law validity in the range 0.294-2.94 μg mL^{-1}. The molar absorptivity and Sandell's Sensitivity are calculated and found as $1.00x10^4$ l mol^{-1} cm^{-1} and 0.00581μg cm^{-2}. The composition of the complex has 1:1 and stability constant of the complex was calculated as 8.38 x 10^4. The effect of various diverse ions also incorporated. The amount of cobalt present in some alloy steel samples was determined by the present method and the results obtained were compared with certified values, the results are quite encouraging compared with certified values.

Keywords: 2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone, Cobalt (II), Spectrophotometry, alloy steel samples.

INTRODUCTION

Cobalt is a ferromagnetic, silver-white, hard, lustrous and brittle element. It is a member of group VIII of the periodic table. The compounds containing cobalt in +2 oxidation state are known to exist. Like iron, it can be magnetized. It is similar to iron and nickel in its physical properties. The element is active chemically, forming many compounds. Cobalt is stable in air and unaffected by water, but is slowly attacked by dilute acids. Cobalt is used in many alloys (super alloys for parts in gas turbine, aircraft engines, corrosion resistant alloys, high-speed steels, cemented carbides), in magnets and magnetic recording media, as catalyst for the petroleum and chemical industries, as drying agent for paints and inks. Cobalt blue is an important part of artists' palette and is used by craft workers in porcelain, pottery, stained glass, and enamel jewellery. The radioactive isotope, cobalt-60, is used in medical treatment and also to irradiate food, so as to preserve it.

Health effects of cobalt: As cobalt is widely dispersed in the environment, humans may be exposed to it by breathing air, drinking water and eating food that contains cobalt. Skin contact with soil or water that contains cobalt may also enhance exposure. Cobalt is not often freely available in the environment, but when cobalt particles are not bound to soil or sediment particles, the uptake by plants and animals is higher and accumulation in plants and animals may occur.

Cobalt is beneficial for humans because it is a part of vitamin B_{12}, which is essential for human health. Cobalt is used to treat anemia in pregnant women, because it stimulates the production of red blood cells. The total daily intake of cobalt is variable and may be as much as 1 mg, but almost all will pass through the body unabsorbed, except that in vitamin B_{12}.

When plants grow on contaminated soils they will accumulate very small particles of cobalt, especially in the parts of the plant we eat, such as fruits and seeds. Soils near mining and melting facilities may contain very high amounts of cobalt, so that the uptake by humans through eating plants can cause health effects.

Analytical chemistry of cobalt: A large number of organic compounds were reported as analytical reagents for the determination of cobalt. These include oximes, phenyl hydrazones, azo compounds etc. 1-Nitroso-2-napthol, proposed by llinsky et al [1] was one of the first organic analytical reagents employed for the determination of cobalt. This reagent along with its isomer, 2-Nitroso-1-napthal was used for the spectrophotometric determination of cobalt in several real samples [2-4]. Many reports are available for the spectrophotometric determination of cobalt. Some of the recent references are listed here. Syama Sundar and his coworkers [5] employed 1-(benzimidazole-2-yl) ethanone thiosemicarbazone for the extractive spectrophotometric determination of Co(II). A sensitive spectrophotometric method for the determination of Co(II) using 1-methyl,2-acetyl benzimidazole thisemicarbazone was reported [6]. Chiranjeevi et al [7] developed a facile, rapid and economical flow injection method for the spectro photometric determination of Co(II) using 3,5-dibromosalicylaldehyde thiosemicarbazone and applied the method for its determination in various environmental samples. Tejam and Thakkar [8] employed 1-phenyl 1,2-butane dione dioxime as a new reagent for the extractive spectrophotometric determination of Co(II) at trace levels. Reddy [9] proposed cyanex 923 for the extractive spectrophotometric determination of Co(II) in synthetic and pharmaceutical samples. A selective method for the FIA spectrophotometric determination of Co(II) based on the use of pyridoxal 4-phenylthiosemicarbazone as reagent was developed by Enrique Cristofol de Alcaraz et al [10]. Gonez Ariza [11] and his coworkers used picolinaldehyde 4-phenyl-3-thiosemicarbazone for the spectrophotometric determination of small amounts of cobalt in the presence of iron.

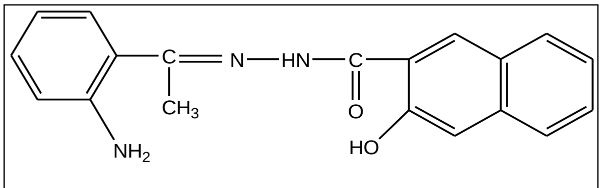
The sensitive spectrophotometric method for the determination of cobalt using 2-(2-Quinolinylazo)-5-diethyl amino benzoic acid has developed by Liang Wang [12]. Z. Li and co-workers [13] reported a method for the spectrophotometric determination of cobalt using 2-(2-quinalinylazo)-5-dimethyl-aminobenzoic acid as a new chromogenic reagent. Eskandari and karkaragh [14] have developed a method for facile spectrophotometric determination of cobalt using alpha-benzilmonoxime. A. Safavi et al [15] has developed a method for indirect kinetic spectrophotometric determination of cobalt based on the redox reaction with Fe(III) in the presence of 1,10- phenanthroline. Oliver R. Hunt et al [16] developed a method for spectrophotometric determination of cobalt with sulfosalicylic acid. Demetrius G. Themelis et al [17] developed a selective method for the spectrophotometric determination of Co(II) using 2,2-dipyridyl-2-pyridylhydrazone and flow injection method. R.S. Lokhande, N.G. Jain, and N. Sari et al [18] developed a selective spectrophotometric determination of Co (II) using 5-Nitrosalicylaldehyde Thiosemicarbazone. M. Magalali Raju and K. Ramakrishna et al [19,20] developed spectrophotometric determination of Co (II) using 3,4-dihydroxy benzaldehyde-1-(3- chloro-2-quinoxalinyl) hydrazone.

The authors have developed a sensitive, selective and rapid method for the spectrophotometric determination of cobalt using 2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone (AHNH).

MATERIALS AND METHODS

Instrumentation: The absorbance and pH measurements were made on a Perkin Elmer UV Lamda 50 double beam spectrophotometer (UV-Visible) controlled by a computer fitted with 1cm path length quartz cells and an ELICO digital pH meter of (Model LI 613) respectively.

Reagents and Chemicals: Preparation of 2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone (AHNH). Equimolar solutions of 2-amino acetophenone in methanol and 3-hydroxt-2-naphthoic hydrazide in hot aqueous ethanol were refluxed for two h on water bath and cooled. The yellowish brown colored solid obtained. It was then filtered, washed and dried. The product showed a melting point of 274-276^{0}c which was found to be different from those of the reactants indicating the formation of the new product.



2-aminoacetyl3-hydroxy-2-naphthoic hydrazone

Fig.1. Structure of ligand

Cobalt (II) solution: 0.01 M solution of cobalt (II) was prepared by dissolving 0.237 g of cobalt chloride in 100 ml volumetric flask with distilled water and 1 or 2 drops of concentrated sulphuric acid. Lower concentrations were prepared by appropriate dilution of the stock solution with distilled water.

Adherence of the systems to Beer's law: To ascertain the sensitivity of the colour reactions and to explore the possibility of determining micro amounts of metal ions, the following procedure is adopted. Varying known aliquots of metal ion solutions are added to a set of 10ml volumetric flasks, each containing 5 ml of buffer solution of desired pH, known volume of DMF and the necessary excess of the reagent solution. The contents of the flasks are brought up to the mark with distilled water and the absorbencies of the solutions are measured at the analytical wavelength against the reagent blank. A plot of absorbance and amount of metal ion (μ g mL^{-1}) is constructed. The slope and the intercept of the plot are computed. The molar absorptivity is calculated from the slope.

Job' method: To a series of 10 ml volumetric flasks, each containing 5 ml of buffer solution of desired pH and known volume of DMF, equimolar solutions of metal ion and the reagent are added in different volume proportions, such that the total volume of the mixture is held constant. The absorbance of each solution is measured at the wavelength of maximum absorbance or at an appropriate wavelength against buffer blank. A plot between mole fraction of the metal ion (V_M / V_M + V_L) or (C_M / C_M + C_L) and the absorbance is made from which the composition of the complex is computed.

Mole ratio method: 5ml of buffer solution and known volume of metal ion solution and varying of the reagent solution are added. The contents of each flask are brought up to the mark with distilled water. The absorbance of each solution is measured at the selected wavelength against the corresponding reagent blank or a blank containing 5ml of buffer solution and required volume of DMF. From the plot between the absorbance and the volume of the reagent, the composition of the complex is ascertained.

RESULTS AND DISCUSSION

Absorption spectra of the reagent and the experimental solution: The absorption spectra of the reagent solution against corresponding buffer (pH 2.0) and that of the complex solution against the reagent blank are recorded in the wavelength range 405 nm to 500 nm respectively. The typical spectra are presented in fig 2.

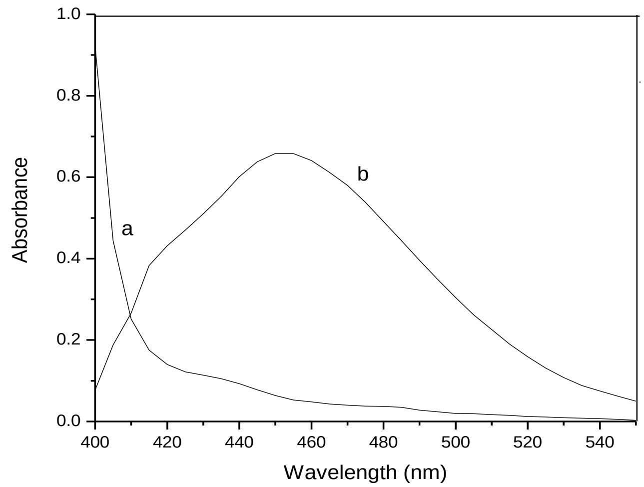


Fig.2. Absorption spectra of a) AHNH Vs buffer blank b) [Co (II)] – AHNH Vs reagent blank, [Co (II)] = 1.0×10^{-3}, M: [AHNH] = 1.0×10^{-2} M, pH = 2.0

The spectra presented in fig.2.show that the complex has an absorption maximum at 450 nm. The reagent has negligible absorbance at 450 nm. Hence, further analytical studies are made at 450 nm.

Effect of AHNH concentration on the absorbance of the experimental solution: The optimum concentration of AHNH required to obtain maximum absorbance is arrived at the results are presented in table 1.

Table.1. Effect of AHNH concentration on the absorbance of experimental solutions [Co (II)] = 1.0×10^{-5} M: pH=2.0: λ=450 nm

[Co(II)] : [AHNH]	Absorbance
1 : 02	0.569
1 : 05	0.634
1 : 10	0.688
1 : 15	0.698
1 : 20	0.697
1 : 25	0.700

The results in table 1indicate that 15 molar excess of the reagent is necessary for achieving maximum absorbance. Hence, the same ratio is maintained throughout the studies.

In Bear's law to explore the possibility of employing the colour reaction for the determination of cobalt (II) keeping the reagent concentration constant, the absorbance of experimental solutions is measured at 450 nm. The results are presented in the form of a plot of absorbance vs amount of Co (II) and shown in fig.3. The straight line plot obtained obeys the equation A_{450}=0.0657C+0.0016. The linear plot between the absorbance and the amount of Co (II) (fig.3.) indicates that Beer's law is obeyed in the range of 0.294-

2.946 μ g mL^{-1} of Co (II). The molar absorptivity and Sandell's sensitivity are $1.00 \pm 0.002 \times 10^4$ 1 mol^{-1} cm^{-1} and 0.0058 μg cm^{-2} respectively. The standard deviation of the method for ten determinations of 2.94 μg mL^{-1} of Co (II) is 0.009. The correlation coefficient (γ) of the calibration equation for the experimental data is 0.9995.

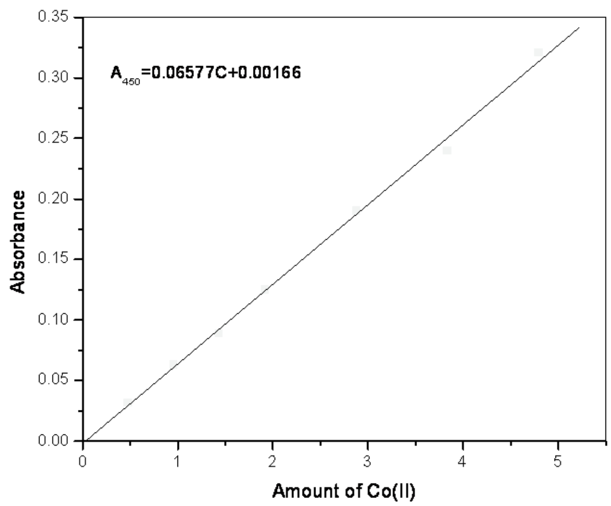


Fig.3. Absorbance Vs amount of Co (II) (μg mL^{-1}), [AHNH] = 1.0×10^{-4} M, pH=2.0; λ= 450nm

In Job's method equimolar solutions (3×10^{-3}M) of cobalt (II) and AHNH are prepared and mixed in different volume proportions keeping the total volume of the mixture constant. The results are presented in fig.4. From the plot it is seen that the composition of the complex is 1:1 and the stability constant β as calculated from the job's method is 8.38×10^4**.**

Mole ratio method carried out from a series of solutions containing 0.5 ml of Cobalt (II) (3×10^{-3}M) solution and different volumes of AHNH solution employed. The results are presented in fig.5. The mole ratio plot confirms the composition as 1:1 [Co (II): AHNH].

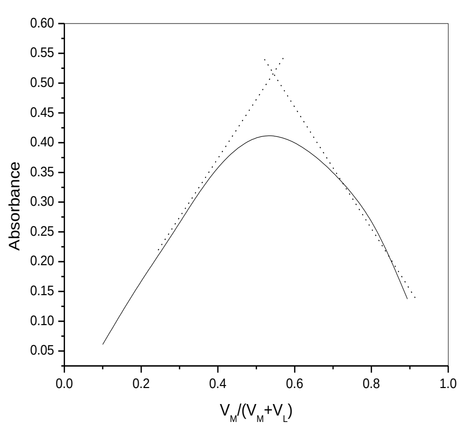


Fig.4. Job's curve
[Co (II)] = AHNH =3×10^{-3}M
pH= 2.0; λ=450 nm

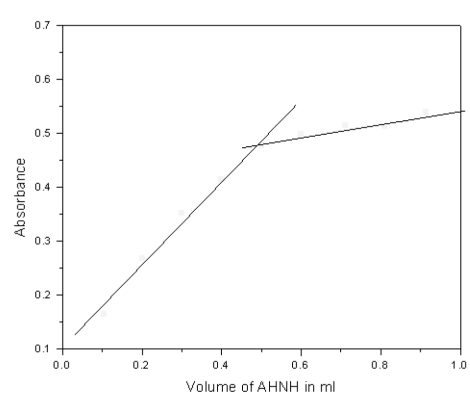


Fig.5. Mole ratio plot
[Co (II)]= [AHNH] = 3×10^{-3}M
pH= 2.0; λ =450 nm

APPLICATIONS

The present method for the determination of cobalt (II) is applied to steel and alloy samples. The amount of Co (II) present is determined as follows.

Procedure: Into a series of 10 mL volumetric flasks, each containing 5.0 ml of buffer solution (pH,2.0), 1.0 ml of 0.1 M of citrate [to mask Ti(IV) and Fe(III)] solution, known aliquots of the sample solution and 1.0 ml of the reagent (1×10^{-2} M) solution are added and made up to the mark with distilled water. The absorbance of these solutions is measured at 450 nm. From the measured absorbance the amount of cobalt (II) is computed by referring to preconstructed calibration plot at 450 nm. The results are presented in table 2.

Table 2: Determination of Co (II) in alloy and steel samples

Sample	Composition(%) certified	Composition(%) Found*	Relative error (%)
Nickel-based high temperature alloy			
i) Udimetz – 500[a]	4.80	4.78	+0.41
ii) Udimet-700[b]	5.20	5.23	-0.57

* Average of seven determinations. Composition of samples (%)
(i) Ni 18.5: Cr 18: Mo 4.8: Al 2.9: Ti 2.9: C 0.08: B 0.006: Zr 0.05.
(ii) Ni 18; Mo 5.21; Cr 1.5; Al 4.3; Ti 3.5; C 0.08; B 0.003

CONCLUSIONS

The colour reaction between cobalt (II) and AHNH. Cobalt (II) forms light pink coloured water soluble complex at pH 2.0. The complex shows absorption maximum at 450 nm. Various parameters such as effect of pH, reagent concentration and interference of associated foreign ions on the colour formation of cobalt (II) – AHNH complex are studied. Beer's law is obeyed in the range of 0.294-2.94 µg mL^{-1}. The composition of the complex is determined by Job's method and molar ratio method. The mole ratio plot confirms the composition as 1:1 [Co (II):AHNH]. The method is applied for the determination of cobalt (II) in steel and alloy samples.

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